

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 September 2002 (26.09.2002)

PCT

(10) International Publication Number
WO 02/074760 A1

(51) International Patent Classification⁷: C07D 315/00

(21) International Application Number: PCT/US02/07878

(22) International Filing Date: 14 March 2002 (14.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/276,581 16 March 2001 (16.03.2001) US

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i)) for all designations
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/074760 A1

(54) Title: PRODUCTION OF 5-METHYLBUTYROLACTONE FROM LEVULINIC ACID

(57) Abstract: A process for producing 5-methylbutyrolactone from levulinic acid utilizing an optionally supported metal catalyst is described. The catalyst has both a hydrogenation and a ring-closing function.

TITLE

PRODUCTION OF 5-METHYLBUTYROLACTONE FROM LEVULINIC ACID

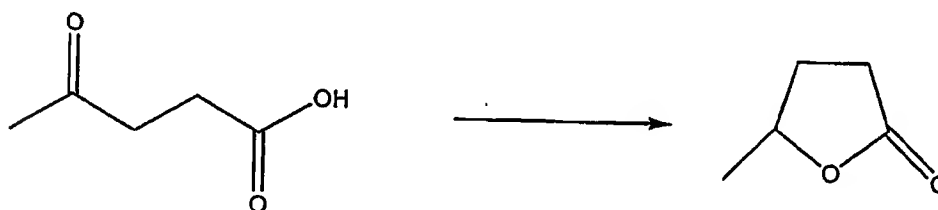
FIELD OF INVENTION

This invention relates to a process for producing 5-methylbutyrolactone from levulinic acid utilizing an optionally supported metal catalyst.

BACKGROUND

Levulinic acid is a well-known product of hexose acid hydrolysis, and is inexpensively obtained from cellulose feedstocks. Consequently, it is an attractive starting material in producing many useful 5-carbon compounds such as methyltetrahydrofuran and derivatives.

5-methylbutyrolactone, also known as 5-valerolactone or γ -valerolactone, can be produced from levulinic acid as shown below.



US Patent No. 5,883,266 discloses the use of a bifunctional catalyst having a first function of hydrogenating and a second function of ring opening to prepare a variety of products from levulinic acid including 5-valerolactone. U.S. Patent No. 2,786,852 disclosed production of 5-valerolactone from levulinic acid using a reduced copper oxide catalyst. U.S. Patent No. 4,420,622 discloses preparation of 5-alkyl-butyrolactones from levulinic esters using metal catalysts.

SUMMARY OF THE INVENTION

The present invention is a process of preparing 5-methylbutyrolactone comprising heating levulinic acid in the presence of hydrogen with a catalytic amount of a catalyst having a hydrogenation and a ring-closing function, wherein the catalyst is a metal. The metal catalyst is optionally supported on a catalyst support. Preferably, the catalyst

support is selected from the group consisting of carbon, SiO₂, and Al₂O₃. The more preferred catalyst support member is carbon. The most preferred catalyst support member is oxidatively stable carbon.

5 The metal catalyst of the invention can be selected from the group consisting of Group VII (Groups 8-10) of the Periodic Table of Elements, preferably selected from the group consisting of iridium, palladium, platinum, rhenium, rhodium and ruthenium and combinations thereof. More preferably the metal catalyst is ruthenium; most preferably supported on oxidatively stable carbon.

10 The process of the instant invention is preferably performed at a temperature from about 100°C to about 200°C, more preferably at a temperature of about 140-160°C. The process is also preferably performed at a pressure of about 0.5 to about 10.0 MPa, more preferably at a pressure of about 4.0 to about 6.0 MPa. The process is also
15 preferably carried out in a liquid phase.

The catalyst of the instant invention may optionally be promoted with at least one promoter, preferably where the promoter is a metal. Preferably, the promoter is selected from the group consisting of Group VII (Groups 8-10) and Group IB (Group 11) elements of the
20 Periodic Table of Elements, more preferably gold, silver and copper.

DETAILED DESCRIPTION OF THE INVENTION

The invention is directed to a process for the preparation of 5-methylbutyrolactone, also known as 5-valerolactone or γ -valerolactone,
25 from levulinic acid in the presence of a metal catalyst.

The catalyst of the invention can include one or more metals selected from Group VIII (Group 8-Group 10) elements from the Periodic Table of Elements, more preferably, the group consisting of iridium, palladium, platinum, rhenium, rhodium and ruthenium. The metal catalyst
30 can optionally be supported on a catalyst support. The metal can be deposited on the support using any method known in the art. Preferably, the catalyst has about 1% to about 10% by weight of metal present on the support; more preferably about 5%.

Optionally, the catalyst can include one or more promoters.
35 Preferably the promoter is also a metal, where the promoter is present in less than about 50 weight percent compared to the metal catalyst. More

preferably the promoter is a Group VIII or a Group IB (Group 11) metal of the Periodic Table of Elements.

Each catalyst individually has both a hydrogenation and a ring-closing function; that is, the reaction proceeds in one step and produces
5 little or none of the pentyl alcohols such as pentanediol.

The catalyst support can be any solid, inert substance including, but not limited to, metal oxides such as silica, alumina, and titania, and carbons. Preferred are carbons with a surface area greater than
200 m²/gm. The catalyst support can be in the form of powder, granules,
10 pellets, or the like.

"Oxidatively stable carbon" is hereby defined as carbon that exhibits substantial weight stability when heated in air. Such carbons are described further in International Publication WO 97/30932. More particularly, when the carbons are heated in air at 125°C for 30 minutes,
15 followed by heating at 200°C for 30 minutes, followed by heating at 300°C for 30 minutes, followed by heating at 350°C for 45 minutes, followed by heating at 400°C for 45 minutes, followed by heating at 450°C for 45 minutes and finally followed by heating at 500°C for 30 minutes, the carbons employed for the process of this invention lose less than 20% of
20 their weight. This sequence of time and temperature conditions for evaluating the effect of heating carbon samples in air is defined herein as the "WVC Temperature Test". The WVC Temperature Test may be run using thermal gravimetric analysis (TGA). Carbons which when subjected to the WVC Temperature Test lose about 20% of their weight, or less, are
25 considered to be advantageously oxidatively stable. Carbon from any of the following sources are useful for the process of this invention; wood, peat, coal, coconut shells, bones, lignite, petroleum-based residues and sugar. Commercially available carbons which may be used in this invention include those sold under the following trademarks: Bameby &
30 Sutcliffe™, Darco™, Nuchar™, Columbia JXN™, Columbia LCK™, Calgon PCB™, Calgon BPL™, Westvaco™, Norit™ and Barnaby Cheny NB™.

The process is best performed at from about 50°C to about 250°C, preferably 100°C to about 200°C, and more preferably at about 140°C to
35 about 160°C. The process is performed at a pressure of about 5 to about 100 atmospheres (0.5 MPa to 10 MPa). Preferably the process is performed at a pressure of about 40 to about 60 atmospheres (4.0 to

6.0 MPa). The process is performed in an atmosphere of pure hydrogen gas, or a mixture of hydrogen with inert gases.

The process is preferably carried out in a liquid phase. The choice of solvent is not critical provided the solvent is not detrimental to catalyst, reactant and product. A preferred solvent is dioxane or 5-valerolactone. Preferred reactor designs are trickle bed and slurry.

The following Examples further illustrate the invention.

Materials and Methods

The following abbreviations and definitions are used herein:

LA Levulinic acid
5-MGBL 5-methyl-gamma-butyrolactone

Catalyst supports used are listed below. The oxidatively stable carbon catalyst supports were tested for weight stability via thermogravimetric analysis according to the WVC Temperature Test.

<u>Support</u>	<u>Weight loss</u>	<u>Source</u>
Sibunit carbon	1.6%	Boreskov Inst. of Catalysis, Novosibirsk, Russia
Silica grade 55	n.a.	W. R. Grace & Co., Columbia, MD
Calsicat carbon	14.9%	Englehard Corp., E. Windsor, CT
Calgon PCB carbon	49%	Nalco Chemical Co., Naperville, IL
Al ₂ O ₃	n.a.	Harshaw Chemical Co., Cleveland,

OH

EXAMPLES

The catalysts were prepared by impregnating the catalyst support by incipient wetness with a metal salt. The precursors used were NiCl₂·6H₂O (Alfa Aesar, Ward Hill, MA), Re₂O₇ (Alfa), PdCl₂ (Alfa), RuCl₃·xH₂O (Aldrich, Milwaukee, WI), H₂PtCl₆ (Johnson Matthey, Ward Hill, MA), 5% Rh using RhCl₃·xH₂O (Alfa), Re₂O₇ (Alfa) and IrCl₃·3H₂O (Johnson Matthey). The samples were dried and reduced at 400°C in H₂ for 2 hours. The reaction was performed by placing the feedstock, 1 mL of a 50% solution of levulinic acid in dioxane with the listed amount of catalyst in a 2 ml pressure vessel. The vessel was charged with H₂ to 800 psi (5.5 MPa) for Examples 1-22 and 700 psi (4.8 MPa) for Examples 23-32, and heated to 215°C for 2 hours. The sample was then

cooled and vented and the product analyzed by GC-MS using methoxyethylether as an internal standard. Results are shown in Table 1 below. The column termed "LA Con" refers to LA Conversion, which is measured by subtracting the remaining amount of levulinic acid from the initial amount of levulinic acid (LA initially-LA remaining).

TABLE 1

Ex.	H ₂ (psi)	Catalyst	5-MGBL Sel (%)	LA Con (%)	Feedstock (mg)	Catalyst (mg)
1	700	5% Ir / Al ₂ O ₃	70.3	36.3	974.5	103.2
2	700	5% Ir / Calgon C	96.7	31.4	979.3	103.8
3	700	5% Ir / Calsicat C	98.1	40.4	972.8	98
4	800	5% Ir / Calsicat C	98.5	98.7	986.4	100.9
5	800	5% Ir / Calsicat C	95.4	99.4	990.1	101
6	700	5% Ir / Sibunit C	95.1	40.8	984.8	106.1
7	800	5% Ir / Sibunit C	97.0	67.3	998.2	99.8
8	800	5% Ir / Sibunit C	96.9	63.5	989.9	100.7
9	700	5% Ir / SiO ₂	85.7	19.9	986.3	101.7
10	800	5% Pd / Calgon C	89.0	15.7	967.5	99.1
11	800	5% Pd / Calsicat C	92.4	32.1	982	100.4
12	800	5% Pd / Calsicat C	96.8	69.4	976.6	98.6
13	800	5% Pd / Calsicat C	91.5	66.8	991.8	99.7
14	800	5% Pd / Sibunit C	82.2	16.3	981.3	102.3
15	800	5% Pd / SiO ₂	67.0	17.7	1028.5	99
16	800	5% Pt / Calgon C	72.1	25.3	1017.8	105.8
17	700	5% Pt / Calsicat C	82.5	15.6	940.7	99.7
18	800	5% Pt / Sibunit C	81.8	18.4	958.1	97.7
19	800	5% Pt / SiO ₂	71.9	19.0	981.9	97.2
20	700	5% Re / Calgon C	83.2	7.8	970	97.6
21	700	5% Re / Calsicat C	82.3	8.9	961	97.9
22	700	5% Re / Sibunit C	76.4	11.1	957	102.2
23	800	5% Rh / Al ₂ O ₃	81.0	52.8	962.3	103.3
24	800	5% Rh / Calgon C	96.1	62.1	989.9	105.2
25	700	5% Rh / Calsicat C	97.6	30.7	934.8	100.4
26	800	5% Rh / Calsicat C	96.0	99.9	990.6	100.9
27	800	5% Rh / Calsicat C	96.1	100.0	986.1	98.3
28	800	5% Rh / Sibunit C	82.1	54.8	982	102.7

Ex.	H ₂ (psi)	Catalyst	5-MGBL Sel (%)	LA Con (%)	Feedstock (mg)	Catalyst (mg)
29	800	5% Rh / Sibunit C	97.3	97.6	993	102.2
30	800	5% Rh / Sibunit C	97.5	96.4	990.1	100.8
31	800	5% Rh / SiO ₂	83.9	43.3	993.2	97.4
32	800	5% Ru / Al ₂ O ₃	64.7	42.3	999.9	96.8
33	800	5% Ru / Calgon C	88.5	57.5	1010	103.2
34	800	5% Ru / Calgon C	73.2	32.6	974.6	10.5
35	800	5% Ru / Calgon C	67.6	59.9	975.1	10.7
36	800	5% Ru / Calsicat C	92.2	81.0	987.6	97.8
37	800	5% Ru / Calsicat C	73.5	50.0	1002	10
38	800	5% Ru / Calsicat C	76.0	65.1	980.7	10.2
39	800	5% Ru / Calsicat C	97.0	100.0	985.2	100.9
40	800	5% Ru / Calsicat C	94.2	100.0	996.5	97.8
41	800	5% Ru / Sibunit C	97.4	52.0	990.1	105.2
42	800	5% Ru / Sibunit C	81.5	31.5	975.7	10.2
43	800	5% Ru / Sibunit C	80.9	47.9	974.7	10.8
44	800	5% Ru / Sibunit C	97.7	97.3	980.4	100
45	800	5% Ru / Sibunit C	98.5	98.3	988.6	100.1
46	800	5% Ru / SiO ₂	81.6	37.1	1010.9	99.3

CLAIMS

What is claimed is:

1. A process for preparing 5-methylbutyrolactone comprising heating levulinic acid in the presence of hydrogen and a catalytic amount of a metal catalyst, said metal catalyst having both a hydrogenation and a ring-closing function.
2. The process as recited in Claim 1 wherein the metal catalyst is supported on a catalyst support.
3. The process as recited in Claim 2, wherein the catalyst support is selected from the group consisting of carbon, SiO₂, and Al₂O₃.
4. The process as recited in Claim 3, wherein the carbon is oxidatively stable.
5. The process as recited in Claim 1, wherein the metal catalyst is selected from the group consisting of Group VIII of the Periodic Table of Elements.
6. The process as recited in Claim 1, wherein the metal catalyst is selected from the group consisting of platinum, rhenium, ruthenium, rhodium, iridium, palladium, and combinations thereof.
7. The process as recited in Claim 6, wherein the metal catalyst is ruthenium.
8. The process as recited in Claim 7, wherein the carbon is oxidatively stable.
9. The process as recited in Claim 1, wherein said process is performed at a temperature from about 100°C to about 200°C.
10. The process as recited in Claim 1, wherein said process is performed at a temperature of about 140°C to about 160°C.
11. The process as recited in Claim 1, wherein said process is performed at a pressure of about 0.5 MPa to about 10.0 MPa.
12. The process as recited in Claim 1, wherein said process is performed at a pressure of about 4.0 MPa to about 6.0 MPa.
13. The process as recited in Claim 1, wherein the process is carried out in a liquid phase.
14. The process as recited in Claim 1, wherein the metal catalyst is optionally promoted with at least one promoter.
15. The process as recited in Claim 14, wherein the promoter is a metal.

16. The process as recited in Claim 15, wherein the promoter is selected from the group consisting of Group VIII and Group IB elements of the Periodic Table of Elements.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 02/07878

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07D315/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 883 266 A (DOUGLAS C. ELLIOT) 16 March 1999 (1999-03-16) cited in the application the whole document	1-9, 13, 14
X	GB 896 949 A (BASF) 23 May 1962 (1962-05-23) claims; examples 9, 10, 16, 17	1-5
X	US 2 368 366 A (LUCAS P. KYRIDES) 30 January 1945 (1945-01-30) page 1 -page 4	1, 2, 9
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents: <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*S* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">12 July 2002</div>	Date of mailing of the international search report <div style="text-align: center;">26/07/2002</div>	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <div style="text-align: center;">Francois, J</div>	

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/07878

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KNOOP: "UBER DIE NATÜRLICHE SYNTHESSE DER AMINOSÄURE" HOPPE-SEYLER'S Z. PHYSIOL. CHEM., vol. 148, 1925, pages 294-315, XP001086670 DE page 309 -page 314	1-3,5,6
A	H.A.SCUETTE: "NORMAL VALEROLACTONE.III." JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., vol. 52, 1930, pages 3010-12, XP002205942 AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC., US ISSN: 0002-7863 page 3010 -page 3011	1-6,9,13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/07878

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5883266	A	16-03-1999	NONE	
GB 896949	A	23-05-1962	NONE	
US 2368366	A	30-01-1945	NONE	